

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
11 January 2001 (11.01.2001)

PCT

(10) International Publication Number  
**WO 01/01787 A2**

- (51) International Patent Classification<sup>7</sup>: **A23D** Yoshihiro [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640-8580 (JP).
- (21) International Application Number: **PCT/JP00/04359**
- (22) International Filing Date: **30 June 2000 (30.06.2000)** (74) Agents: **FURUYA, Kaoru** et al.; Hamacho-Hanacho Building 6th Floor, 2-17-8, Nihonbashi-Hamacho, Chuo-ku, Tokyo 103-0007 (JP).
- (25) Filing Language: **English**
- (26) Publication Language: **English** (81) Designated States (national): **BR, CA, CN, US.**
- (30) Priority Data:  
11/184762 30 June 1999 (30.06.1999) **JP** (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).
- (71) Applicant (for all designated States except US): **KAO CORPORATION** [JP/JP]; 14-10, Nihonbashi-Kayabacho 1-chome, Chuo-ku, Tokyo 103-0025 (JP).
- Published:**  
— Without international search report and to be republished upon receipt of that report.
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **MASUI, Kenji** [JP/JP]; Kao Corporation, Research Laboratories, 2-1-3, Bunka, Sumida-ku, Tokyo 131-8501 (JP). **KONISHI,**
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



**WO 01/01787 A2**

(54) Title: **WATER-IN-OIL TYPE EMULSIFIED FAT AND/OR OIL COMPOSITION**

(57) Abstract: The present invention provides a water-in-oil type emulsified fat and/or oil composition which comprises a diglyceride and which is excellent in a flavor release during the time for ingestion thereof. That is, the present invention provides a water-in-oil type emulsified fat and/or composition which is composed of (1) the aqueous phase based on water and (2) the oil phase comprising 15 % by weight or more, based on the total oils and fats, of diglycerides, the composition including a flavor component(s), 30 % by weight or more of the said emulsified composition being able to be reversed in phase within one minute after it has been introduced into water at 36 °C.

## DESCRIPTION

## WATER-IN-OIL TYPE EMULSIFIED FAT AND/OR OIL COMPOSITION

## Technical Field

The present invention relates to a water-in-oil type emulsified fat and/or oil composition which comprises a diglyceride and which is excellent in a flavor release during the time for ingestion thereof. The water-in-oil type emulsified fat and/or oil composition of the present invention is preferably and suitably utilized in a margarine, a fat spread, a butter cream, a shortening, etc.

## Background Art

In recent years, the intake of lipid in eating habits in various developed countries is increasing to raise the concentration of triglycerides (neutral fat) in blood and to cause obesity, and this has been a major cause of Life style related disease.

Diglyceride has been revealed to be a fat or oil, after which is eaten, which hardly increases the concentration of a neutral fat in blood and hardly constitutes a body fat (JP-A 10-176181). Therefore, the diglyceride is expected to be used as the substitution of a conventional fat or oil in a (water-in-oil emulsion) food having a large amount of the fat or oil such as a

cooking oil, in particular, a margarine and a spread.

Various water-in-oil type emulsified compositions containing a diglyceride blended with a fat and/or oil are proposed, for example, in JP-B 7-121196, JP-A 3-91441, US-A 4284655, JP-A 61-63242, US-A 5879735, WO 95/22257, WO 96/32022 and the like, but there is no description of a flavor release from the flavor component thereof.

The present inventors have further continued in the investigation of the water-in-oil type emulsified fat and/or oil composition. As the result, they found the problem that the foods containing diglycerides in the high concentration during the time for ingestion and the foods are not good in flavor release related directly to the degree of good taste thereof. This phenomenon is not observed in a fat and/or oil being mainly based on a triglyceride.

#### Disclosure of the Invention

The present inventors have found that in a system of the water-in-oil type emulsion containing diglycerides in the high concentration, emulsification is so stable that the rate of the phase reversal of the emulsion from W/O type to O/W type in the mouth delays, thus affecting much of the flavor release.

The present invention provides a water-in-oil type emulsified fat and/or oil composition which is composed of (1) the aqueous phase based on

water and (2) the oil phase of fat and/or oil comprising 15 % by weight or more, based on the total oils and fats, of diglycerides, and the composition including a flavor component(s), 30 % by weight or more of the said emulsified composition being able to be reversed in phase within one minute after it has been introduced into water at 36 C°. Thus, the above-mentioned problem of the prior art has been solved.

Further, the fat(s) and/or oil(s) of the present invention comprise preferably 15 to 90 % by weight of diglycerides and 85 to 10 % by weight of triglycerides. The composition of the present invention may comprise 0.05 to 20 % by weight, preferably 0.1 to 10 % by weight, of flavor components.

#### Modes for Carrying Out the Invention

The fatty acid constituting the diglyceride used in the present invention includes a C<sub>6</sub> to C<sub>22</sub> saturated or unsaturated fatty acid, preferably a C<sub>16</sub> to C<sub>22</sub> unsaturated fatty acid. In the fatty acid group which is contained in the diglyceride, an unsaturated fatty acid is desirable in the amount of 55 % by weight or more.

As the starting fat or oil used in the diglyceride, a fat or oil containing a large amount of an unsaturated fatty acid-residue, for example, including a vegetable (or plant) fat or oil such as safflower oil, olive oil, cottonseed oil, rapeseed oil, corn oil, soybean oil and palm oil; further, an animal fat or oil such as lard, beef-tallow and butter; and a fractional oil thereof, a transesterified oil thereof and a hydrogenated oil (hardened oil) thereof may

be used. The diglyceride is obtained by ester-exchanging reaction (,ester-interchanging reaction or transesterification) of a mixture of one or more of these fats and oils and glycerol in the presence of a catalyst or by ester-exchanging reaction of a mixture of a fatty acid composition having the high levels of unsaturated fatty acids and glycerol in the presence of a catalyst.

An excess of monoglycerides formed in a mixture of the generated diglycerides can be removed by a molecular distillation method or a chromatography method. The remaining monoglycerides are desirably removed to make it as small as possible. When the content thereof is 5 % by weight or less (preferably 2 % by weight or less), there is no problem.

From the viewpoint of the stability in the emulsification, the content of diglycerides in the present invention is preferably 15 % by weight or more, particularly preferably 15 to 90 % by weight based on the amount of the fats and oils. The content is particularly preferably 45 % by weight or more from the viewpoint of controlling triglycerides in blood and inhibiting the accumulation of body fat.

The flavor component referred to in the present invention means all additives, related to tastes and aromas, such as perfumes, tasting agents (proteinous materials, amino acids etc.), spices, salts and sugars, and these are blended in an aqueous phase and/or an oil phase.

The degree of the phase reversal referred to in the present invention can be confirmed by means of the concentration of the flavor component blended in the aqueous phase in water, when 5 g of the emulsified fat and/or oil composition was dispersed in 50 g of water with a magnetic stirrer (with a bar of 2.5 cm in length, revolved at 300 rpm) at a controlled temperature of 36 °C in a beaker having its capacity of 100 ml. For example, in case a salt is placed as a flavor component, the degree of the phase reversal is represented in terms of the concentration of the salt in water after the emulsified composition have been dispersed in water at an oral temperature (about 36 °C) for one minute, given that the recognized salt concentration in water is made to 100 when demulsification is carried completely out by heating. If a sugar is placed as a flavor component, the concentration of the sugar may be measured by the same way as those in mentioned above. It is desired that 30 % or more, preferably 50 % or more and particularly preferably 80 % or more of the emulsion is made to reverse in phase for an initial one minute. When the degree of the phase reversal is less than 30 %, the strength of the flavor release is considerably low and the start of the release delays.

The composition exhibiting such a physical property can also be prepared even by selecting an ordinarily used formulation ingredient and an amount thereof. However, the demulsifier shown below (which is not ordinarily used in a W/O type emulsion) is

advantageously used in order to easily obtain such a composition.

The demulsifier referred to in the present invention is an additive functioning as a flavor enhancer or a flavor release-enhancer, which makes the phase reverse rapidly in the mouth during the time for ingestion, without affecting the stability in the emulsification during storage, to realize the excellent flavor release.

As the demulsifier, a polyglycerol fatty acid ester, a water-soluble decomposed protein, lysolecithin, a sucrose fatty acid ester, a monoglyceride organic acid ester and a sorbitan fatty acid ester described below may be used.

The polyglycerol fatty acid ester should be a mono-, di- or poly- ester of a saturated or unsaturated fatty acid having 10 to 22 carbon atoms, wherein the fatty acid constitutes the polyglycerol fatty acid ester, and polyglycerol and it should have HLB of 7 or more (preferably 11 or more). If the HLB is less than 7, the flavor release is worsened on the contrary.

As the decomposed protein, one or more kinds obtained by decomposing a milk protein, a vegetable (or plant) protein, an egg protein or the like with an enzyme or acid may be used. Specifically, the milk protein for use includes casein, lactalbumin, lactoglobulin, lactoferrin, whey (or milk serum), skim milk powder (or non-fat milk powder), whole milk powder, butter milk powder, milk serum protein, milk etc. The plant protein includes soybean

protein, wheat protein, corn protein etc. The egg protein includes ovalbumin, conalbumin, ovomucoid, ovoglobulin, egg white protein, yolk protein, whole egg protein etc.

As a preferable physical property of the decomposed protein obtained by decomposing one of these, water solubility is mentioned. If they are water-insoluble, the flavor release is worsened on the contrary due to gelation of the protein. Further, the decomposing treatment is carried preferably out before blending but it may be carried out during or after emulsification.

The lysolecithin is a water-soluble compound constituted from a fatty acid being a  $C_{10}$  to  $C_{22}$  saturated or unsaturated fatty acid and it has HLB of 8 or more (preferably 12 or more). If the HLB is less than 8, the flavor release is worsened on the contrary.

The sucrose fatty acid ester should be a mono-, di-, or poly-ester of a saturated or unsaturated fatty acid having 10 to 22 carbon atoms, wherein the fatty acid constitutes the sucrose fatty acid ester, and sucrose; and it should have HLB of 5 or more (preferably 8 or more). If the HLB is less than 5, the flavor release is worsened on the contrary.

The monoglyceride organic acid ester is one having 1 or 2 organic acids bonded to a monoglyceride constituted of a saturated or unsaturated fatty acid having 10 to 22 carbon atoms and it should have HLB of 8 or more. If the HLB is less than 8, the flavor release is worsened on the contrary.



The sorbitan fatty acid ester should be constituted from a saturated or unsaturated fatty acid having 10 to 22 carbon atoms, and it should have HLB of 8 or more. In particular, one of polysorbates known as Tween series from Atlas Ltd. in United States of America, including polyoxyethylene sorbitan monostearate (Tween 60), polyoxyethylene sorbitan tristearate (Tween 65), polyoxyethylene sorbitan monooleate (Tween 80), polyoxyethylene sorbitan monolaurate (Tween 20) and polyoxyethylene sorbitan monopalmitate (Tween 40) can be preferably used. Incidentally, if the HLB is less than 8, the flavor release is worsened on the contrary.

The value determined by the formula of Griffin was used as HLB of the polyglycerol fatty acid, monoglyceride organic acid ester or sorbitan fatty acid ester, while the value measured by the emulsification method was used as HLB of lysolecithin or the sucrose fatty acid ester.

It is important that the demulsifier is added in such an amount as to exhibit the action of demulsification (effect of improving the flavor release). Although the demulsifier is preferably added to the aqueous phase, there is no problem if it is added to the oil phase. Its approximate amount is within the range of 0.01 to 5 % by weight, preferably 0.1 to 1 % by weight, in the composition.

The starting material of an edible fat or oil used in the

present invention may be one or more selected from vegetable fats and oils including soybean oil, rapeseed oil, palm oil, corn oil, cottonseed oil, coconut oil and palm kernel oil; and animal fats and oils including lard, fish oil and milk fat; and those obtained by hydrogenation or ester-exchange of these oils, for use.

The solid fat content (SFC) in the oil phase used in the present invention may be usually within the range of 1 to 35 at 5 to 35 °C, preferably 7 to 30 at 20 °C and preferably 1 to 20 at 30 °C.

The water-in-oil type emulsified fat and/or oil composition of the present invention may be prepared in a usual manner, and the ratio of the aqueous phase based on water to the oil phase by weight can be made within the range of the oil phase : the aqueous phase = 20 : 80 to 85 : 15 (preferably 40 : 60 to 85 : 15).

A dairy product, an emulsifier or the like as a sub-component in the oil phase may be blended with the composition of the present invention. Further, milk protein, starch, a thickening polysaccharide, a thermoplastic protein (gelatin etc.) or the like may be blended with the aqueous phase based on water.

Further, an anti-oxidant including tocopherol, an ascorbyl ester such as palmitate and stearate, a tea leaf, a herb such as rosemary, a natural anti-oxidizing component extracted from a leaf or a root of a peach may be used together in order to inhibit the deterioration of the water-in-oil type emulsified fat and/or oil

composition.

### Examples

#### [Preparation of the diglyceride]

While the fatty acid obtained from a soybean oil (obtained by wintering at 0 °C) and glycerol were mixed at the molar ratio of 2 : 1, they were reacted at 70 °C for 3 hours in the presence of a catalyst as a commercial lipase preparation of immobilized 1,3-position-selective lipase (Lipozyme 3A™ provided by Novo Industry A. S.). During the reaction, the inside pressure of the system was reduced to 0.26 kPa in order to remove water formed by esterification. After the lipase preparation was removed by filtration from the reaction product, the filtrate was subjected to molecular distillation, decoloration and deodorization to obtain the diglyceride (consisting of diglyceride content of 85 % by weight, monoglyceride content of 1.3 % by weight and triglyceride content of 13.7 % by weight and having open tube melting point of 5 °C).

#### Examples 1 to 5 and Comparative Examples 1 to 4

According to the recipe of Table 1, the compositions were emulsified at 70 °C for 10 minutes by a homogenizing mixer (Tokushu Kika Kogyo Co., Ltd.) to make the plastic emulsion 800 g after the reaction. The obtained emulsion was rapidly cooled and plasticized in a usual manner whereby a water-in-oil type

emulsified fat and/or oil composition was produced.

The degree of phase reversal of the obtained water-in-oil type emulsified fat and/or oil composition was measured in the following manner.

Namely, after 50 g of water was placed in a beaker having its capacity of 100 ml and was adjusted to 36 °C, 5 g of the emulsified fat and/or oil composition was dispersed therein with a magnetic stirrer (with a bar of 2.5 cm in length, revolved at 300 rpm). The salt concentration in the water was measured with time. The degree of phase reversal was made as  $(\text{salt concentration in water after one minute}) \div (\text{salt concentration upon complete demulsification}) \times 100$ . Then, a compact meter C-121 (Horiba, Ltd.) for a salt content was used for the measurement of the salt concentration. The results are shown in Table 1.

Then, the obtained water-in-oil type emulsified fat and/or oil compositions (the product just after preparation and the product after storage at 5 °C for 30 days) were evaluated in viewpoint of their flavor release upon eating in mouth under the following criteria by special panelists (10 panelists). The average points are also shown in Table 1.

The evaluation criteria are as follows.

- 4: The flavor release is very good.
- 3: The degree of the flavor release is slightly weak and the start of the release delays slightly.

2: The degree of the flavor release is extremely weak and the start of the release delays.

1: The degree of the flavor release is extremely bad and the start of the release delays extremely.

Table 1

	Examples	Comparative Examples			
		1	2	3	4
Oil phase (parts)	Diglyceride	48.9	48.9	48.9	48.9
	Partially hydrogenated (hardened) palm oil (IV = 40)	21.0	21.0	21.0	21.0
	Stearic acid monoglyceride	—	—	—	—
	Additive 1 type	—	—	—	—
	Vitamin E	0.02	0.02	0.02	0.02
	$\beta$ -Carotene	0.002	0.002	0.002	0.002
	Butter flavor	0.1	0.1	0.1	0.1
	Cheese flavor	—	—	—	—
	Distilled water	27.9	27.9	27.9	27.9
	Additive 2 type	A	B	C	D
Aqueous phase (parts)	Skim milk powder	0.3	0.3	0.3	0.3
	Common salt	1.3	1.3	1.3	1.3
	Fresh cream	—	—	—	—
	Degree of phase reversal (%)	100	100	100	100
Flavor release (just after production)		4	4	4	4
Flavor release (after storage)		4	4	4	4

SFC in the oil phase in Examples 1 to 4 and Comparative Examples 1 to 4 was 15.3 at 20 °C or 8.8 at 30 °C; and SFC in the oil phase in Example 5 was 9.8 at 20 °C or 6.0 at 30 °C.

- A: Decomposed whey protein (provided by Morinaga Milk Industry Co., Ltd.)
- B: Sucrose fatty acid ester having HLB of 15 (F-160, provided by Dai-Ichi Kogyo Seiyaku Co., Ltd.)
- C: Polyglycerol fatty acid ester having HLB of 15 (ML-750, provided by Sakamoto Yakuhin Kogyo Co.; Ltd.)
- D: Polyglycerol fatty acid ester having HLB of 11 (SO-750, provided by Sakamoto Yakuhin Co., Ltd.)
- E: Whey protein (provided by Morinaga Milk Industry Co., Ltd.)
- F: Sucrose fatty acid ester having HLB of 1 (F-10, provided by Dai-ichi Kogyo Seiyaku Co., Ltd.)
- G: Polyglycerol fatty acid ester having HLB of 4.5 (Sunsoft Q-175S, provided by Taiyo Kagaku Co., Ltd.)

## CLAIMS

- 1, A water-in-oil type emulsified fat and/or oil composition which is composed of (1) the aqueous phase based on water and (2) the oil phase of fat and/or oil comprising 15 % by weight or more, based on the total oils and fats, of diglycerides, and the composition including a flavor component(s), 30 % by weight or more of the said emulsified composition being able to be reversed in the phase within one minute after it has been introduced into water at 36 C° .
- 2, The water-in-oil type emulsified fat and/or oil composition as claimed in Claim 1, which comprises a demulsifier.
- 3, The water-in-oil type emulsified fat and/or oil composition as claimed in Claim 2, wherein the demulsifier is at least one member selected from the group consisting of a polyglycerol fatty acid ester having HLB of 7 or more, a water-soluble decomposed protein, lysolecithin having HLB of 8 or more, a sucrose fatty acid ester having HLB of 5 or more, a monoglyceride organic acid ester having HLB of 8 or more, and a sorbitan fatty acid ester having HLB of 8 or more.
- 4, The composition as claimed in Claim 1, wherein the fat and/or oil comprises 15 to 90 % by weight of diglycerides and 85 to 10 % by weight of triglycerides.
- 5, The composition as claimed in Claim 1, which comprises 0.1 to 10 % by weight of a flavor component.